

THE IMPROVEMENT OF ZINC ELECTRODES FOR ELECTROCHEMICAL CELLS

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GODDARD SPACE FLIGHT CENTER
CONTRACT NAS 5-9591

LEESONA MOOS LABORATORIES
GREAT NECK, NEW YORK

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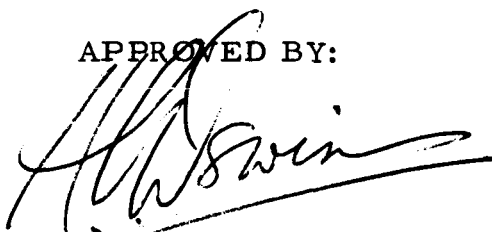
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APPROVED BY:



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ABSTRACT

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A further investigation has been made of the parameters which govern the growth of mossy and crystalline dendrites. It was found that the transition from one type of growth to the other occurred at a critical current density corresponding to the onset of diffusion control. Under ambient conditions this critical current density was 20 ± 2 mA/cm². This finding was further confirmed by an analysis of the temperature dependence of the growth process.

The effect of temperature on the deposit's adherency was also examined. Temperature does not affect adherency when the electrodeposition is diffusion controlled. For activation controlled electrodeposition, the adherency decreases with temperature. In addition, at increased temperature, dendrite growth is initiated after fewer coulombs have passed.

A study on trickle-charging has been initiated.

author

SECTION I - INTRODUCTION

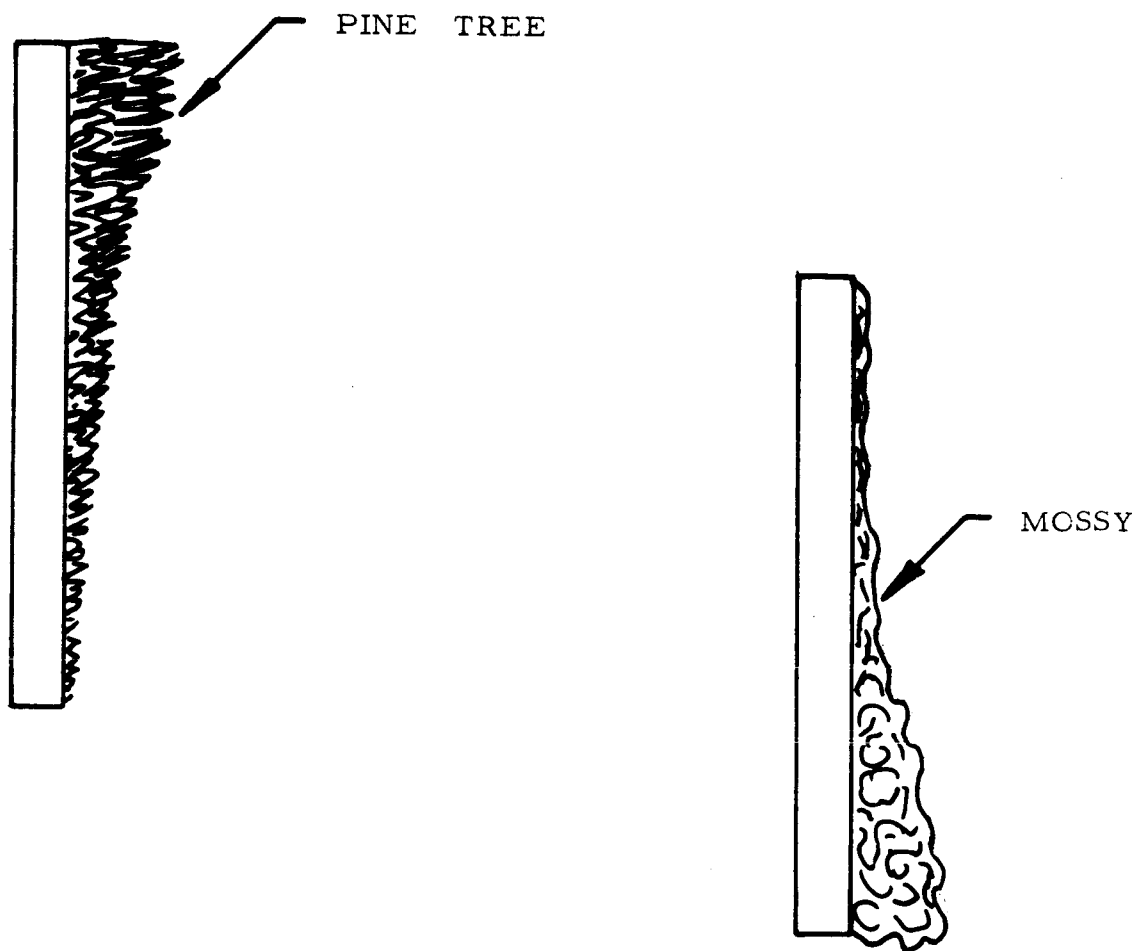
The present Contract NAS 5-9591 is a continuation of an earlier study on Contract NAS 5-3908. The aim of this contract is to extend our understanding of dendrite growth. It is expected that the results of this investigation will lead to improvements in both the manufacture and handling of silver/zinc batteries.

During the first quarter, evidence was gathered which indicated that the mossy type of dendrite growth is associated with "activation control" while the more crystalline dendrite growth corresponds to "diffusion control". The effect of density gradients caused by depletion of zincate at a vertical electrode surface during deposition was demonstrated. This was demonstrated in experiments using vertical electrodes where it was found that propagation of the mossy growth was greatest in the region of highest zinc availability, i. e., at the bottom of the electrode. On the other hand, propagation of crystalline dendrites, which is favored by conditions of depletion, was found to be most marked at the top of the electrode. These effects are illustrated in Figure 1.

Diffusion-controlled zinc deposition at constant current was found to be accompanied by potential oscillations. These oscillations were explained in terms of the stirring effect brought about by hydrogen evolution when the potential falls to cathodic values. The use of intermittent charging as a means of obtaining a more adherent deposit was found to be effective during diffusion-controlled electrodeposition but to have no influence on the activation-controlled process. This finding confirms the theory that the advantage of this type of charging is mainly due to disruption of the diffusion layer.

During the second quarter, the effect of temperature has been investigated. Mossy and crystalline growth are affected quite differently by changes in temperature, further illustrating that these morphologies grow by different mechanisms. It has been shown that crystalline dendrites grow under all conditions of diffusion control. Potential oscillations have been used as a means of identifying this type of control.

At the request of the contracting officer, a brief study has been initiated in order to establish optimum conditions for trickle-charging Ag/Zn batteries during wet stand.



EFFECT OF DENSITY DIFFERENCES ON DENDRITE GROWTH
AT A VERTICAL ELECTRODE

Figure 1

SECTION II - DISCUSSION

2.1 EXPERIMENTAL METHODS

2.1.1 Materials

The electrolyte used during this quarter was the same KOH/zincate electrolyte used last quarter, i. e. 43% KOH, 1.13M with respect to zinc.

2.1.2 Electrolysis Cell and Electrodes

Zinc sheet cathodes and the same rectangular cell were used as during the past quarter. In place of the saturated calomel reference electrode (SCE), the mercury, mercury oxide reference was used. This electrode has advantages over the SCE since it is very stable in basic solutions and because a "salt-bridge" error of 0.126V is avoided. The actual measured potential of the $\text{Zn}/\text{Zn}(\text{OH})_4^{2-}$ couple is -1.62V vs SCE. When this value is corrected for the "salt-bridge" error, the result -1.49V vs SCE is found to be in fair agreement with the thermodynamic value⁽¹⁾ of -1.46 vs SCE.

The potential series for the silver zinc battery vs the Hg, HgO reference electrode is given in Appendix A.

2.1.3 Measurement of Dendrite Growth

The adherency of the deposit was again measured by the technique of Romanov.⁽²⁾ This technique was fully described in the previous report.

2.2 EXPERIMENTAL RESULTS

2.2.1 Potential Oscillations and Morphology as a Function of Current Density

In the first quarterly report it was shown that zinc electrodeposition from saturated zincate at 30 mA/cm² is accompanied by periodic rises and falls in the overpotential. (see also Curve 1 of Figure 2) The rising portion of this potential oscillation has been explained by assuming diffusion control and applying the theory of chronopotentiometry at constant current. The period of an oscillation is approximately equal to the transition time, τ , of the Sand equation.⁽³⁾

$$\tau^{1/2} = \frac{n F C D^{1/2} \pi^{1/2}}{2i}$$

As the overpotential is increased, hydrogen discharge at the electrode is accelerated. Gassing at the electrode then provides local stirring and

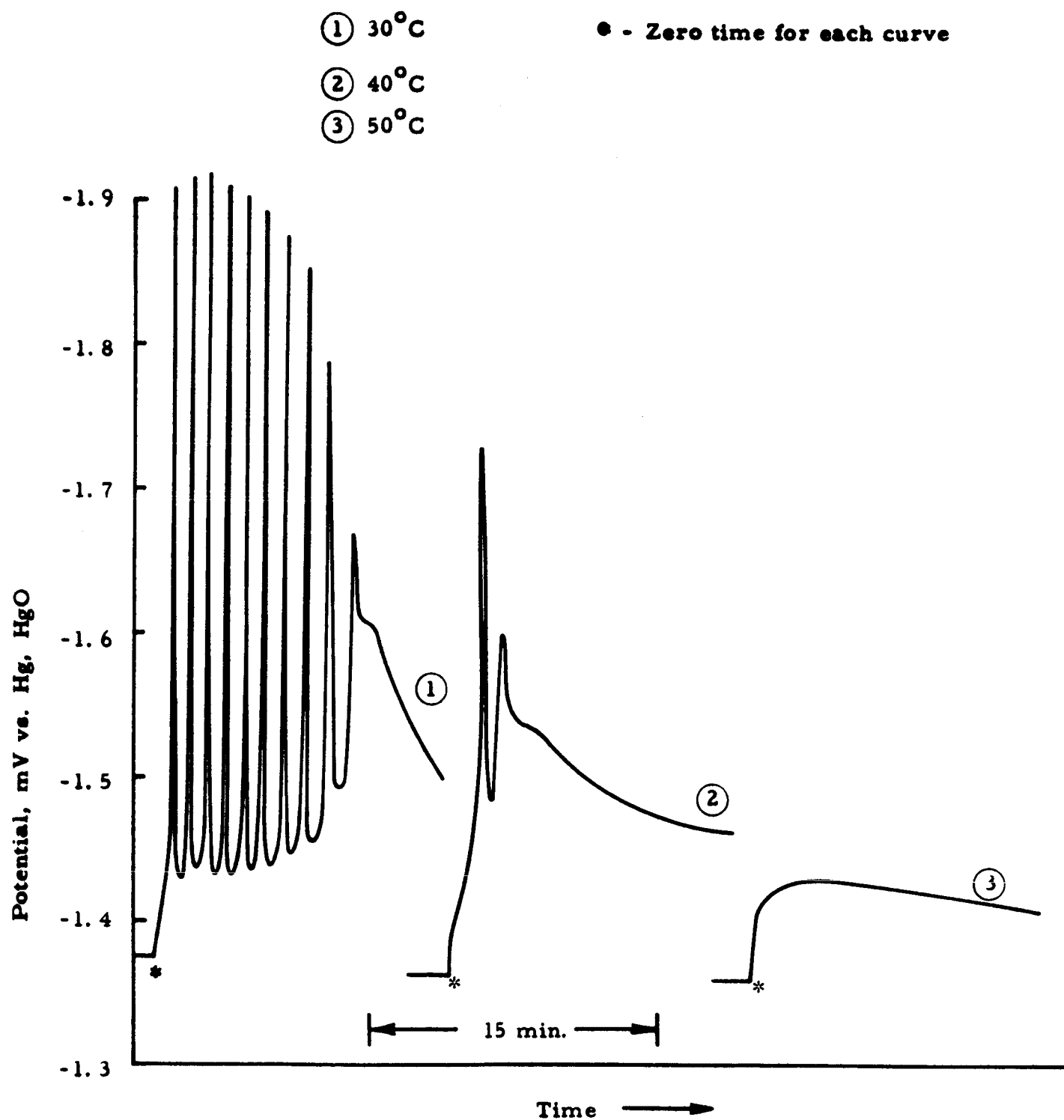


Figure 2. Cathode Potential vs. Time During Electrodeposition of Zn from 43% KOH, 1.13 M Zincate Electrolyte at 30 mA/cm²

a subsequent fall in overpotential is observed. When the reaction is activation-controlled, e. g. at 15 mA/cm², no oscillations are observed.

It was expected that between 15mA/cm² and 30 mA/cm² a critical current density exists corresponding to the transition from mossy to crystalline dendrite morphology - i. e. from activation- to diffusion-controlled electrodeposition. Such a critical current density was observed experimentally.

Deposition was carried out at room temperature at 15, 20, 22, 25 and 30 mA/cm². At the three largest current densities where the process is diffusion controlled, deposition was accompanied by potential oscillations. Diffusion control was verified at the three current densities in excess of the critical current density by agreement between the theoretical and practical values of $i \tau^{1/2}$. The theoretical value of $i \tau^{1/2}$, 0.25 amp sec^{1/2}, was calculated using the value of D obtained polarographically (1.8 x 10⁻⁶ cm²/sec). For the experimental values, τ was taken equal to the initial potential rise time, and the calculated $i \tau^{1/2}$ values are shown in Table I.

TABLE I

$i \tau^{1/2}$ Values for Current Densities Greater Than Critical	
<u>Charging Current Density mA/cm²</u>	<u>$i \tau^{1/2}$ amp sec^{1/2}</u>
22	0.26
25	0.23
30	0.26

At 20 mA/cm², there was only a small (75 mV) rise and fall of the potential over twenty minutes, but no periodic oscillations were observed. Absence of any rapid potential rise in this chronopotentiogram indicates that deposition was no longer entirely diffusion-controlled. Furthermore, both mossy and crystalline dendrite forms were observed on this electrode. In agreement with the previous work, the crystalline dendrites were found at the top of the electrode where the electrolyte was most dilute in zincate, while mossy dendrites formed at the base of the electrode where the zincate concentration was highest. Thus, transition between diffusion control and activation control occurred at about 20 mA/cm². At the lowest current density employed, 15 mA/cm², only mossy dendrites were observed with little corresponding variation in overpotential during deposition.

The current densities quoted are, of course, in terms of the apparent area and do not reflect changes in surface roughness. Changes in surface roughness and zincate concentration (caused by convection) permit only an approximate estimate of the critical current density. Differing

conditions of natural convection and electrode orientation will cause the observed critical current density to vary from one cell geometry to another. For example, an empirical equation relating the critical current density to zincate concentration and electrolyte viscosity for a natural convection cell used by recent workers⁽⁴⁾ predicted a critical current density three times greater than that observed in our present experimental system.

2.2.2 Temperature Studies

The effect of temperature on dendrite growth has been investigated during the present quarter. Temperature should affect the electro-deposition primarily by:

- (a) decreasing the overpotential during activation-controlled electrodeposition
- (b) increasing the diffusion coefficient of zincate and increasing the critical current density.

Both the critical current density and the adherency of the deposit were examined as a function of temperature. Results indicate that temperature is an important factor when deposition is activation-controlled but has little effect when the electrode process is diffusion-controlled.

2.2.2.1 Critical Current Density vs. Temperature

In zinc electroplating from acid baths it is well known that a critical current density exists above which the deposit is compact and below which the deposit is spongy. This critical current density is reported to increase with temperature.⁽⁵⁾ Experiments were conducted to determine whether or not a similar temperature dependence exists in the present alkaline system. Electrodeposition was carried out in the temperature interval 20°C to 50°C at current densities between 5 and 30 mA/cm². A constant amount of charge (27C/cm²) was passed for each cathode sample, which was then examined and classified morphologically. Those samples having mossy dendrites over all or part of the electrode were classed as "mossy" while those classed as "crystalline" contained only the crystalline dendritic deposit. The morphology vs. current density relationship is given in Figure 3.

For reasons given in Section 2.2.1, the critical current density could not be located exactly, but appears somewhere within a transition region (shaded area of figure). From the figure it can be seen that a definite increase in the critical current density with temperature is observed for this system over the temperature range 20 to 50°C.

In addition to the visual appearance of the electrode, the transition with temperature from diffusion to activation control at 30 mA/cm² may be observed in the potential-time relationships observed at 30, 40, and 50°C. In Figure 2 it can be seen that at 30° and 40°C the deposition is diffusion-

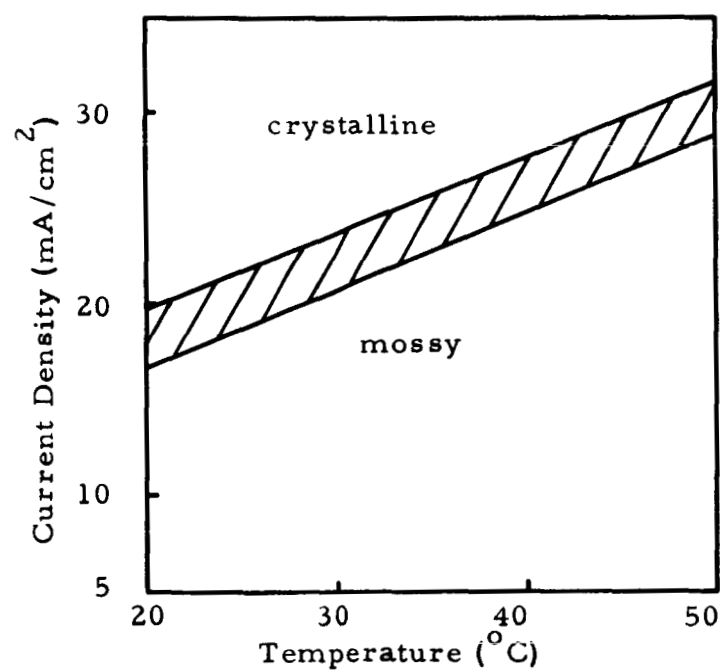


Figure 3. Variation of Critical Current Density (Shaded Area) With Temperature Within Experimental Limits

controlled (shown by the potential oscillations). See Section 2.2.1 for the correlation between potential oscillations and diffusion control. At 50°C, however, the chronopotentiogram is more typical of those obtained during activation-controlled deposition and the deposits on several samples were either partly or completely mossy.

2.2.2.2 Overpotential vs. Temperature

The effect of temperature on the activation-controlled deposition region was to decrease the overpotential. The overpotential decreased by 15mV between 30 and 50°C at 15 mA/cm² charging current.

2.2.3 Adherency

It was shown during the first quarter that a portion of the zinc deposit can be easily removed from the electrode by wiping with a tissue while the remainder of the deposit is strongly adherent. Both mossy and crystalline dendritic deposits may be separated empirically into adherent and non-adherent fractions. Adherency has been studied as a function of (a) total charge passed (coulombs), (b) charging rate, and (c) temperature.

2.2.3.1 Adherency vs. Coulombs

Figure 4 shows data obtained under conditions of diffusion control; Figure 5 shows data obtained under conditions of activation control. In both cases, as deposition continues, an increasingly greater fraction of zinc is deposited non-adherently.

2.2.3.2 Adherency vs. Charging Rate

A given number of coulombs deposited at 30 mA/cm² will, in general, have a different adherency from the same quantity deposited at 15 mA/cm². Compare, for example, data plotted in Figure 4 with isothermal data in Figure 5. In order to determine the relationship between adherency and rate of charge, several zinc electrodes were charged to the same extent (27C/cm²) over a range of rates from 2 to 30 mA/cm². The adherency of each deposit was determined and the data is shown as the solid curve in Figure 6. The overpotential corresponding to these current densities is shown by the broken line in Figure 6, which plots the polarization observed on each test cathode. The general relationship between adherency and charging rate is complex and connected with the morphology of the deposit. The solid curve shown in Figure 6 may be divided into three regions:

- i) where adherency falls with increasing c. d.
- ii) where adherency is at a minimum for a range of c. d., and
- iii) where the adherency is constant (at about 70%) with c. d.

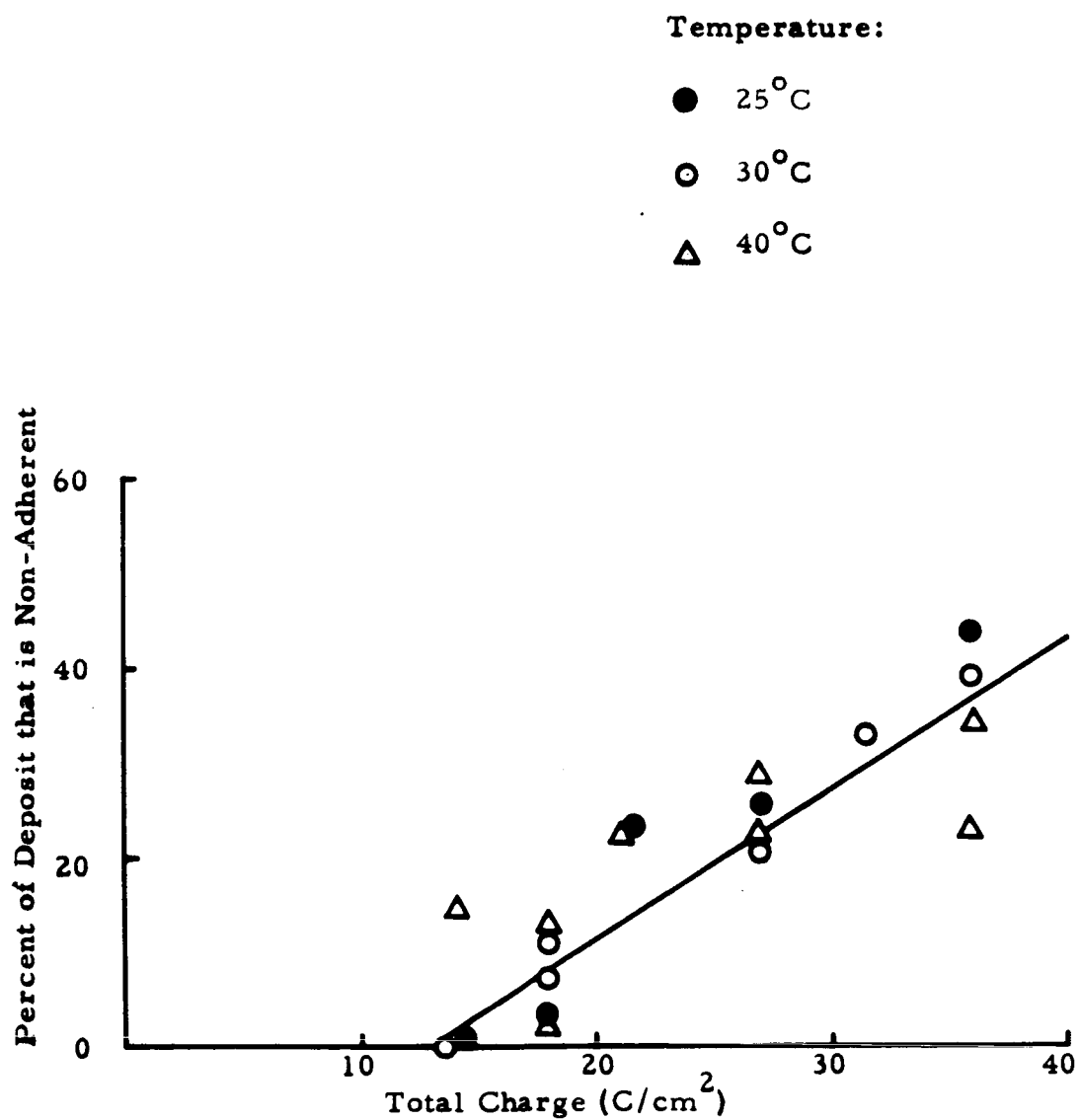


Figure 4. Percentage of the Deposit at 30 mA/cm² Which is Non-Adherent vs. Coulombs Passed

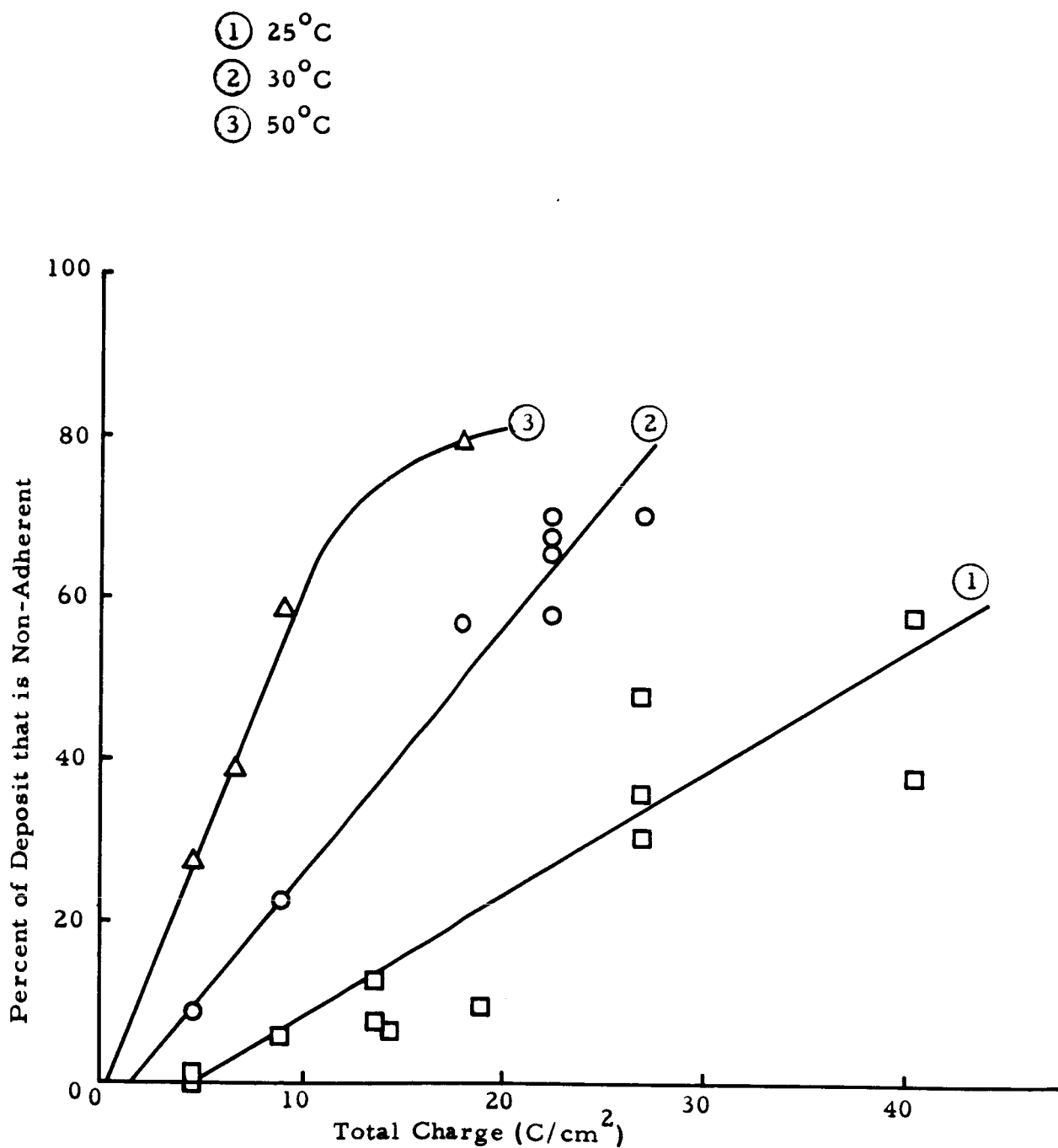


Figure 5. Percentage of the Deposit at 15 mA/cm² Which is Non-Adherent vs. Coulombs Passed.

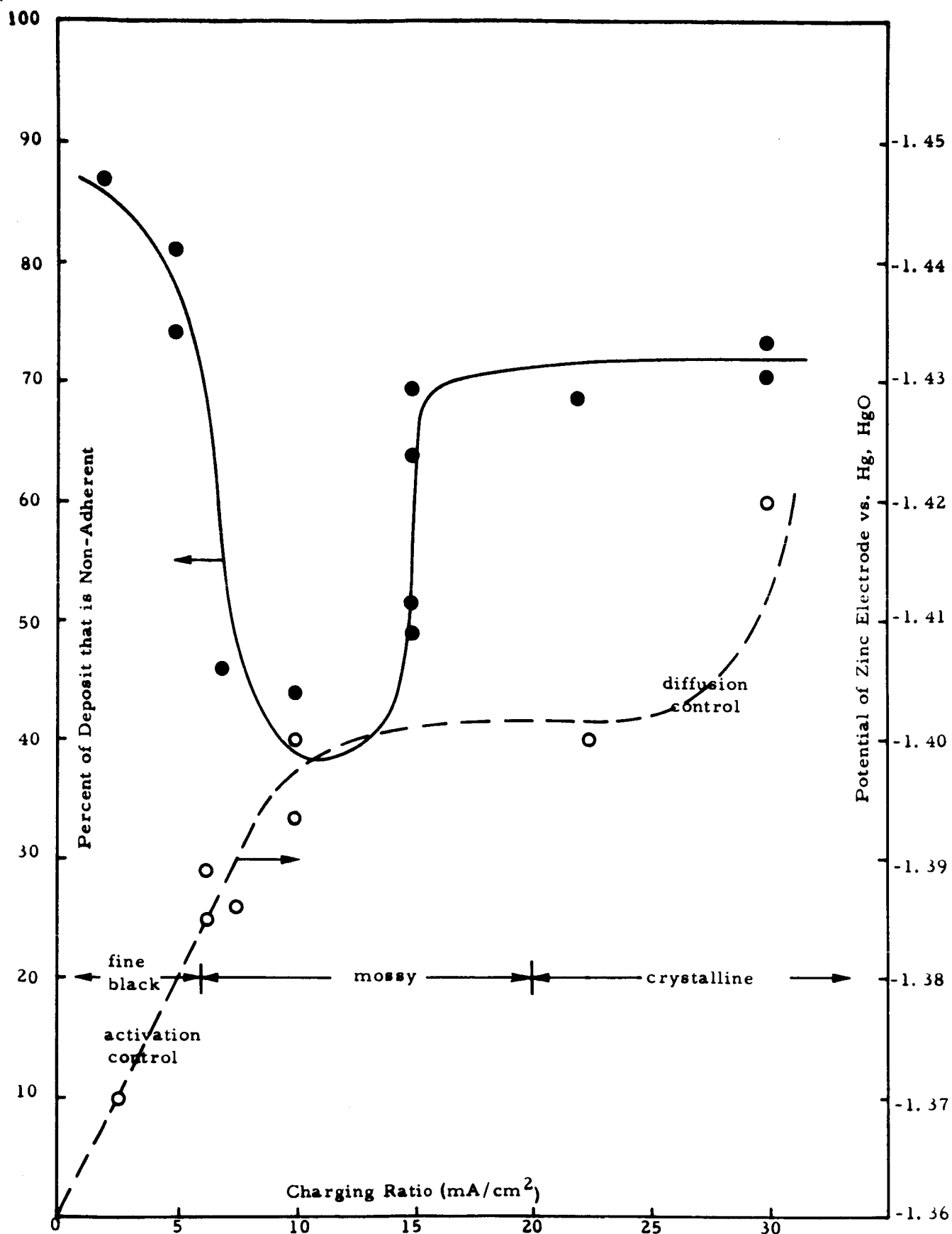


Figure 6.

Adherency of Deposit vs. Charging Rate (mA/cm^2) to $27 \text{ C}/\text{cm}^2$ (solid line) and Electrode Potential vs. Current Density (broken line) 43% KOH, 1.13M Zn, 25°C

These regions also coincide with regions of three different morphologies. In the region of lowest current density (region (i)), the deposit was the most adherent, and a morphology was obtained which has not been described previously. The morphology of region (i) corresponds to polarizations of less than 25mV. The deposit was "fine-black" in appearance. When both mossy and fine black morphologies are formed on the same vertical plate electrode (say at 7mA/cm²), the fine black species is found at the lower part of the electrode. Thus, although both the mossy and fine black morphologies are formed under activation-controlled conditions, the difference in their structure must be attributable to different concentrations of zincate and the effect this has on local overpotentials.

2.2.3.3 Density of Deposit and Propagation Rate

The density of the deposit varies with the morphology. The fine black form is denser than the crystalline form and the latter is still denser than the mossy type. The propagation rate of each type decreases in the order mossy > crystalline > fine black. In terms of current density, within the range 7-20 mA/cm², where mossy dendrites form, the dendrites propagate most rapidly, while in the range below 7 mA/cm² the dendrites propagate most slowly. Dalin and Solomon⁽⁶⁾ measured the rate of propagation of zinc dendrites across a gap filled, in part, by free electrolyte and, in part, by a test cellophane membrane. They found a range of 6-10 mA/cm² in which propagation was most rapid and a range below 6 mA/cm² in which propagation was the least rapid. These workers explain their results in terms of the diffusion rate of zinc through the membrane (low current density region) and efficiency of zinc discharge (high current density region). Their explanations in terms of the membrane are admittedly not very satisfactory when compared to their own calculations. It is suggested that the effect of morphology may have made a significant contribution to their observations.

In a practical cell, shorting occurs when an advancing dendrite contacts the opposite electrode. Based on the propagation rates of the various morphologies it is expected that a large number of coulombs must pass before the fine black deposit would short across, while relatively few coulombs would be required before shorting occurred if mossy dendrites were the propagating form.

2.2.3.4 Adherency vs. Temperature

Adherency has been found to be independent of temperature when the diffusion-controlled deposit is obtained. On the other hand, when electro-deposition is activation-controlled, and mossy dendrites are formed, the adherency of the deposit decreases with increasing temperature.

Over the range of temperatures 25 to 40°C, a crystalline deposit is obtained at 30 mA/cm² (see Figure 3). The w/w% of the non-adherent fraction of this deposit was determined for samples within this temperature range and plotted as a function of coulombs passed in Figure 4. No effect of temperature is apparent.

The relationship between non-adherency of deposit and temperature in the activation-controlled region is shown in Figure 5. Zinc was deposited at 15 mA/cm² over the temperature range 25 to 50°C. As the temperature increases, the adherency decreases for the same number of coulombs passed.

As observed in the previous report, a given number of coulombs must pass before the deposit becomes measurably non-adherent. The initiation of the non-adherent deposit is not a function of temperature when the reaction is diffusion-controlled. When the reaction is activation-controlled, however, the number of coulombs required to initiate the formation of the non-adherent deposit appears to decrease with increasing temperature.

It was predicted that temperature would affect electrodeposition primarily through its effect on the diffusion coefficient and on the overpotential. However, the activation energy for the diffusion process is probably small, and the temperature dependence of the diffusion coefficient is only of the order of 2 percent/°C. (7) Such small deviations would be within the limits of experimental error.

The effect of temperature on the adherency of the activation-controlled deposit is not obvious at this time. It may simply relate to the activation energy of the deposition process or, perhaps, several temperature-dependent processes may be involved, e.g. solubility of zincate or an increase in natural convection as the viscosity decreases. The hydrogen discharge reaction has been postulated⁽⁵⁾ as causing non-adherent deposits of the mossy type and the effect of temperature on this activation-controlled process must also be considered. In this regard it is worth noting that mossy growths are frequently observed around the base of a hydrogen bubble on the electrode surface.

2.2.4 Study of Trickle-Charging of Silver-Zinc Batteries

When Ag/Zn batteries are permitted to stand on open circuit, the reaction, $\text{Zn} + 2\text{H}_2\text{O} + 2\text{OH}^- \rightarrow \text{H}_2 + \text{Zn}(\text{OH})_4^{2-}$ occurs at a finite rate even when the electrode is amalgamated and results in a gradual loss of capacity of the zinc electrode. The discharge reaction can be avoided by imposing a small cathodic current so that anodic zinc dissolution does not occur at a finite rate. Figure 7 shows separate E/i curves for hydrogen evolution and for the zinc/zincate couple. Thus, in order to avoid self-dissolution, the net cathodic current should be chosen such that the potential is maintained a few millivolts cathodic to the true open circuit potential of the zinc/zincate couple.

The trickle-charging current may be selected in the following way. The two potentials A and B shown in the diagram can be determined. A represents a practical zinc structure, and B a heavily amalgamated zinc plate. At the latter electrode, it is expected that the hydrogen over-voltage will be high and the true potential of the zinc/zincate couple will be established (the degree of amalgamation is low enough not to affect the thermodynamic activity of zinc).

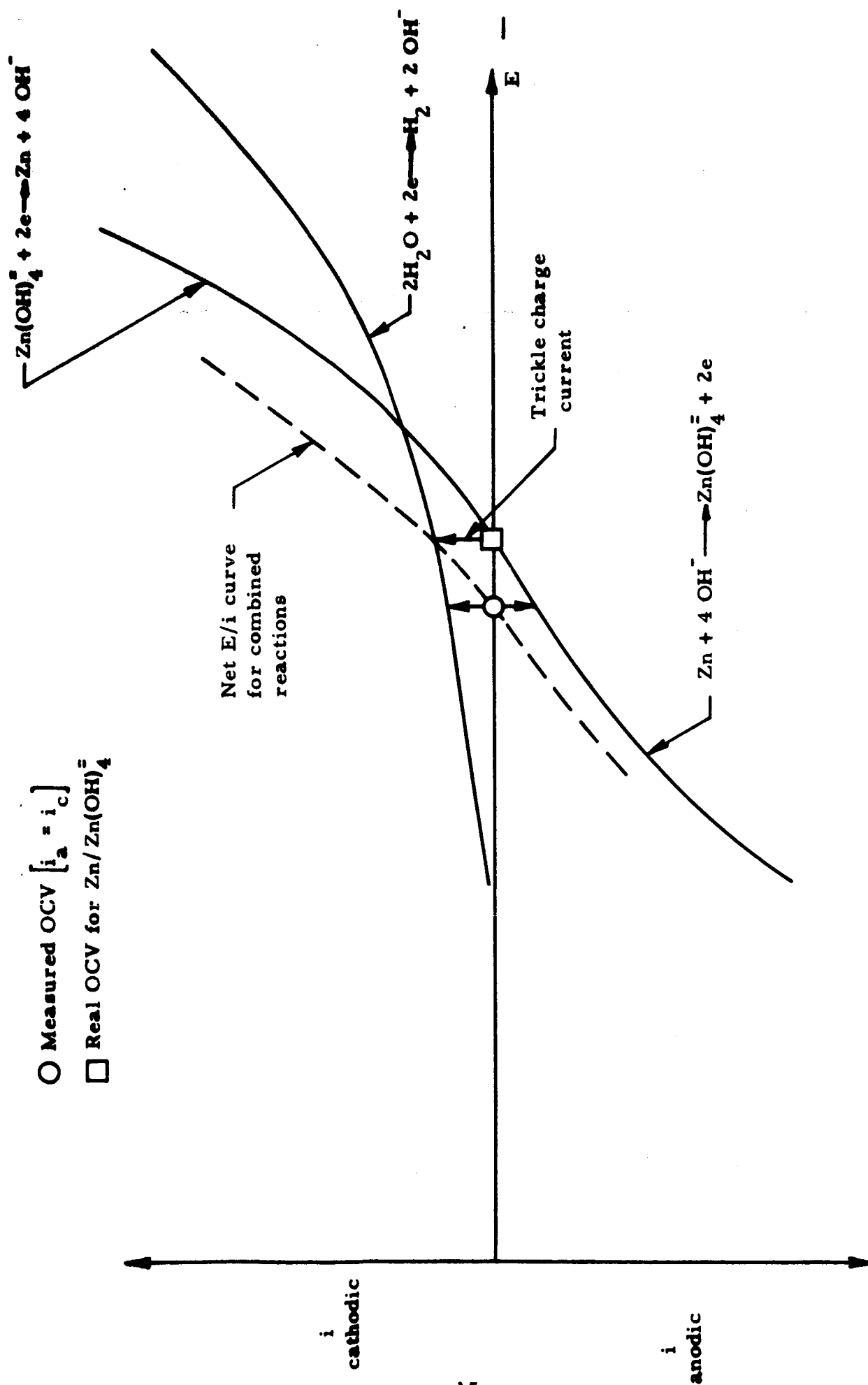


Figure 7. Potential Current Density Relationships Relevant to Self-Discharge of Zinc in KOH

The potential difference (A-B) has been found to be less than 1 mV. It would, therefore, appear that a polarization of 5 mV or less would be sufficient to prevent self-dissolution.

The reduction of oxygen will, of course, occur at the negative plate simultaneously as will the oxidation of hydrogen at the silver electrode. The relative extent of these processes will be dependent on the state of charge of the silver electrode.

SECTION III - NEW TECHNOLOGY

No new technology has been developed during this reporting period.

SECTION IV - PROGRAM FOR NEXT REPORTING PERIOD

During the next quarter, the investigation of trickle-charging will continue. The effect of cathodic polarization of a practical zinc structure in the range 0-5 mV will be determined.

Further work will be carried out on intermittent charging methods. A wide range of pulse frequencies and pulse lengths will be investigated.

SECTION V - CONCLUSIONS AND RECOMMENDATIONS

Correlation of morphology and potential-time data for zinc deposits have shown that crystalline dendrites may be taken as indicative of diffusion-control during electrodeposition. A critical current has been found to exist, below which mossy dendrites begin to form and above which crystalline dendrites form. The effect of temperature on this critical current density has been investigated. A linear increase in critical current density with temperature was found over the range 20 to 50°C.

The adherency of deposits is a function of three variables: coulombs, charging rate, and temperature. In general, adherency decreases with the number of coulombs passed. It varies with charging rate according to the morphology of the deposit obtained. At low charging rates (0-7 mA/cm²) a fine black deposit forms. This morphology was not observed previously. It appears to be the most adherent deposit. At charging rates between 7 and 20 mA/cm² the deposit is least adherent and is of the mossy morphology. When the deposit is crystalline - at charging rates in excess of 20 mA/cm² - its adherency is intermediate between mossy and fine black and rather insensitive to any increase in charging rates above the critical value. Temperature appears to have little or no effect on the adherency of crystalline dendrites. On the other hand, increasing the temperature during growth of mossy dendrites markedly decreases the adherency of the deposit. Increasing the temperature also appears to decrease the number of coulombs which must be passed before non-adherent growth is initiated. An attempt will be made to correlate adherency with more fundamental electrode parameters such as surface capacitance and electrode capacity.

Further investigations are needed before the effects of temperature on the adherency can be fully explained. On this basis, it would appear that battery cycle life (as determined by negative plate capacity) should decrease with increasing temperatures and that some advantage may be gained by low temperature charging. It was also shown that the rate of propagation of the deposit normal to the electrode can be related to the morphology: the most adherent deposit is also the most dense, while the least adherent is least dense. Therefore, that range of current densities which gives rise to the mossy deposit also results in the greatest rate of dendrite propagation.

The low current density charging rates result in the most adherent and most dense deposit and, therefore, represent a preferred condition. Adherency appears to be a major factor which limits both the rate and quantity of charge that a zinc plate can tolerate. That there is a considerable scope for improvement here is indicated by the fact that under some conditions a percentage of non-adherent deposit is always observed.

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APPENDIX A

APPENDIX A

+0.902	Overpotential for O ₂ Evolution at 10 ⁻³ A/cm ² on Ag		
+0.514	Ag ₂ O + 2OH ⁻ = 2 AgO + H ₂ O + 2e		
+0.489	Ag electrode, commercial cell		
+0.303	4OH ⁻ = O ₂ + 2H ₂ O + 4e		
+0.244	2 Ag + 2OH ⁻ = Ag ₂ O + H ₂ O + 2e		
0	Hg, HgO		
-0.926	H ₂ + 2OH ⁻ = 2H ₂ O + 2e		
-1.31	Zn + 4OH ⁻ = Zn(OH) ₄ ⁼ + 2e (theoretical)		
-1.35	Zn + 4OH ⁻ = Zn(OH) ₄ ⁼ + 2e (measured)	MOSSY)
-1.37	Zn electrode, commercial cell) Dendrite
-1.43		PINETREE) Morph-
-1.53		ACICULAR) ology
-1.68	Overpotential for H ₂ Evolution at 10 ⁻³ A/cm ² on Zn		

potential

POTENTIAL SERIES FOR SILVER/ZINC BATTERY